TRANSPORT COEFFICIENTS IN POROUS GRANULAR MEDIA

S. Ya. Bronin, I. G. Busarov,
and V. M. Kolobov

UDC 539.217.1-532.546

Transport coefficients are calculated as functions of porosity using an ordered model of granular porous media. We consider grain-spheres situated at the nodes of various crystalline lattices. The behavior of the transport coefficients at low porosity values is considered. A comparison with experimental data is performed.

Introduction. The dependence of transport coefficients (electrical conductivity ρ, diffusion D, gas permeability K) in porous media upon the porosity φ is often represented in the form of power laws [1]. The best known of these is the experimentally established relationship between σ of a porous medium, the pores of which are filled by an electrolyte with conductivity σ_0, and φ (Archey's law):

$$\frac{\sigma}{\sigma_0} = c_0 \varphi^l, \tag{1}$$

where c_0 is a constant of the order of unity, and l is an exponent which depends weakly on φ. The present study will consider granular porous systems, i.e, those obtained by pressing grains of approximation one size, with form close to spherical. The experimental data of [2] on σ for a medium formed by pressing glass spheres are described over a wide range of φ $(0{,}02 \leqslant \varphi \leqslant 0{,}40)$ by Eq. (1) with variation of l from $l \approx 1.5$ at high φ to $l \approx 2.3$ at low φ. However, power expressions of the form of Eq. (1) for the transport coefficients are approximations, since they do not consider the geometric properties of the concrete porous medium. The character of the $\sigma(\varphi), K(\varphi)$ dependences can be refined by choosing a model for the pore space geometry. We note that at a gas molecule free path length λ much less than the characteristic pore size, the dependence of the effective diffusion coefficient coincides with $\sigma(\varphi)$ in light of the equivalence of the equations describing these processes.

Various models have been used to describe the structure of porous media, including both ordered and unordered ones [3]. In the capillary model of porous media K is expressed by the Carman–Kozeny relationship [1] $K \sim \varphi^3/\omega^2$. However the capillary model does not reflect the true features of pore space geometry in granular porous media, in particular, changes in section of a pore channel along length. The ordered model proposed in [4] is closer to the real geometry of pores in granular porous media. Approximate calculations of $\sigma(\varphi)$ were performed in [4] for such a medium with the assumption that the electrical conductivity of each pore channel, the network of which forms a pore lattice, is proportional to the area of the minimum section of that channel. The functional dependences $\sigma(\varphi)$ obtained in this manner were then normalized to experimental values.

The real granular porous structure which spherical grains packed into a volume form is known as random close packing (RCP, [5]). The RCP structure occupies an intermediate position with respect to φ ($\varphi_{(RCP)} \approx 0{,}36$) between spheres located tangent to each other at the nodes of a simple cubic (SC) lattice and a face-centered cubic (FCC) lattice ($\varphi_{(SC)} \approx 0{,}476$, $\varphi_{(FCC)} \approx 0{,}260$). The RCP structure also occupies an intermediate position with regard to the number N of bond-pores per node: for RCP $N \approx 4$ [4], for SC $N = 6$, and for FCC $N = 4$. These facts permit the proposal that the values of the transport coefficients for RCP at φ values not too low will also lie between those of SC and FCC lattices, which permits estimation of the transport coefficients for RCP.

In the present study we will calculate $\sigma(\varphi)$ and $K(\varphi)$ for various ordered lattices, the structure of which is based on the model of [4], in the approximation:

High-Temperature Institute, Academy of Sciences of the USSR, Moscow. Energy Conservation Problems Institute, Academy of Sciences of Ukrainian SSR, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 61, No. 6, pp. 964-970, December, 1991. Original article submitted April 3, 1991.

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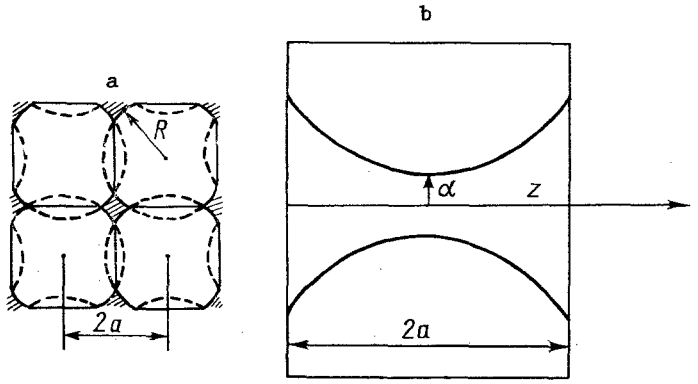

Fig. 1. Granular structure geometry: a) structure for SC lattice (pore space shaded); b) longitudinal section of pore channel.

$$\frac{1}{g} \sim \int \frac{dz}{S(z)}, \quad \frac{1}{k} \sim \int \frac{dz}{S^2(z)}. \tag{2}$$

The error of Eq. (2) can be evaluated by comparison with problems which permit exact solutions. The calculated transport coefficients can be compared to experimental dependences. Together with the ordered model we will evaluate the disorder in the pore structure of real granular porous media responsible for the change in ℓ in Eq. (1) at small φ values. The character of the vanishing of the transport coefficients as $\varphi \to \varphi_c$ (the critical value φ_c corresponds to the point where the pore space ceases to be interconnected) will also be studied.

Model Description. Transport Coefficient Calculation. We will construct lattice models of porous media, the transport coefficients of which we will then compare to coefficients in real granular media. We will describe a model for the example of the SC lattice. The centers of the grains, which initially have a spherical form and are tangent to each other, are located at the nodes of an SC lattice. The distance between the sphere centers is 2a, initially $a = a_0$, and the sphere radius $R = a_0$. Such a situation corresponds to the maximum value of φ. Decrease in a with preservation of the volume of each sphere leads to their deformation and decrease in φ (Fig. 1a). We will assume that at points where the grains do not touch each other, they maintain the form of spheres of radius R. Such grain deformation is an analog of the pressing of real granular porous media.

In this model the pore space is a cubic lattice of identical channels having variable cross section. The critical value φ_c corresponds to vanishing of the minimum channel section S_{min}. The parameter defining φ and the area S of the pore channel cross section is the quantity $\varkappa = R/a$. We will consider change in $\varkappa$ over the range $[1; \sqrt{2}]$. The value $\varkappa = 1$ corresponds to tangency of undeformed spheres, while at $\varkappa = \sqrt{2}$ $S_{min} = 0$. The condition of conservation of grain volume under deformation yields the function $a(\varkappa)$:

$$a(\varkappa) = a_0 \left(\frac{9}{2} \varkappa^2 - 2\varkappa - \frac{3}{2} \right)^{-\frac{1}{3}}. \tag{3}$$

In the case of an SC lattice φ is given by

$$\varphi(\varkappa) = 1 - \frac{\pi}{6} - \frac{\pi}{2}(\varkappa - 1) + \frac{\pi}{4}(\varkappa - 1)^2 + \frac{\pi}{3}(\varkappa - 1)^3, \tag{4}$$

$\varphi(1) \approx 0{,}476$; $\varphi(\sqrt{2}) = \varphi_c \approx 0{,}0349$.

Along the z-axis of the pore channel S(z) varies periodically with a period 2a. The electrical conductivity of the pore structure is defined by the conductivity g of these channels. For $S(\varkappa, z)$ a simple geometric treatment yields ($-a \leq z \leq a$):

$$S = \left(4 - \pi d + 4d \arcsin \sqrt{1 - \frac{1}{d}} - 4\sqrt{d-1} \right) a^2 \quad \text{for } d > 1,$$
$$S = (4 - \pi d) a^2 \quad \text{for } d < 1, \tag{5}$$

where $d=\varkappa^2-z^2/a^2$. For d < 1 are not separated from each other by grains. Since for calculation of the transport coefficients in the approximation of Eq. (2) only the dependence $S(\varkappa, z)$ is important, for convenience we replace the pore channel by a channel formed by a body of revolution about the z-axis with area at the point z equal to $S(\varkappa, z)$ from Eq. (5). The radius of such a channel $r(z)=\sqrt{S(\varkappa, z)/\pi}$, and its longitudinal section is shown in Fig. 1b. We denote r(0) = α, the value corresponding to S_{min}.

Using Eq. (5) we find g and k in the approximation of Eq. (2). For a given pore lattice geometry defined by the grain position (in the given case, the simple cubic lattice) and $\varphi(\varkappa)$ from Eq. (4) we obtain $\sigma(\varphi)$, $K(\varphi)$ of the medium.

We will evaluate the accuracy of the approximation of Eq. (2) by comparison with the exact solution of the problem of resistance of an infinite single-cavity hyperboloid of revolution, the surface of which is given by the equation

$$\frac{\rho^2}{A^2}-\frac{z^2}{B^2}=1, \tag{6}$$

where $\rho^2 = x^2 + y^2$. The resistance of such a hyperboloid can be found by solving the Laplace equation $\Delta V = 0$ in ellipsoidal coordinates [6] with boundary conditions: $V = \pm V_\infty$ at $z = \pm\infty$ and $\partial V/\partial n = 0$ on the hyperboloid surface. The exact solution of such a problem gives the value of the quantity $\tilde{\sigma}_H$, inversely proportional to the hyperboloid resistance, in the form

$$\tilde{\sigma}_H = 2B(\sqrt{\gamma^2+1}-1), \tag{7}$$

whree γ = A/B. The approximate value given by Eq. (2) for the analogous quantity σ_H is:

$$\sigma_H = B\gamma^2. \tag{8}$$

The ratio $\tilde{\sigma}_H/\sigma_H$ obtained from Eqs. (7), (8) characterizes the accuracy of the approximation used.

In a similar manner we can compare the exact value of the gas permeability $\tilde{K}_H$ to the approximation of Eq. (2). To determine $\tilde{K}_H$ of the hyperboloid of Eq. (6) one must solve the equations: $\operatorname{div} v=0$, $\operatorname{grad} P=\eta \operatorname{rot}\operatorname{rot} v$. For the given values $P(z = \pm\infty) = \pm P_\infty$ and the gas flow Q found through the hyperboloid we find $\tilde{K}_H \sim Q/2P_\infty$. For the quantity $\tilde{K}_H$ solution of the problem yields:

$$\tilde{K}_H = \frac{2B^3}{3}((\gamma^2-2)\sqrt{\gamma^2+1}+2). \tag{9}$$

The approximate K_H of Eq. (2) for the hyperboloid of Eq. (6) has the form:

$$K_H = \frac{B^3}{2}\gamma^4. \tag{10}$$

The ratios $\tilde{\sigma}_H/\sigma_H$ and $\tilde{K}_H/K_H$ from Eqs. (7)-(10) are shown as functions of γ in Fig. 2.

We will consider the deviations of the approximation solutions from the exact ones in the region of change of γ, which corresponds to the same range of the parameter h for the two problems: the hyperboloid of Eq. (6) and the ordered lattice described by Eqs. (3)-(5). The parameter h is the ratio of the two radii of curvature of the surface at the point z, corresponding to $S = S_{min}$, i.e., z = 0. For the hyperboloid of Eq. (6) $h_1 = \gamma^2$; for the channel given by Eq. (5) (Fig. 1b) $h_2 = \alpha/R$. In the range considered $\varphi_c \leqslant \varphi \leqslant 0{,}476$ the parameter $0 \leqslant h_2 \leqslant 0{,}4$, which at $h_1 = h_2$ corresponds to $0 \leqslant \gamma \leqslant 0{,}64$. For γ < 0.64 the ratio $\tilde{\sigma}_H/\sigma_H > 0.91$, $\tilde{K}_H/K_H > 0.89$. Thus, in the case considered the approximation of Eq. (2) can be regarded as completely satisfactory.

With grain location at the nodes of other lattices relationships similar to Eqs. (3)-(5) can be obtained, thus yielding $\sigma(\varphi)$, $K(\varphi)$. Results of such calculations and comparison with experimental data from [2] are shown in Figs. 3, 4. We note that the calculated K is written in the form

$$K = a_0^2 F(\varphi), \tag{11}$$

where $F(\varphi)$ is a dimensionless function obtained from Eqs. (3)-(5) in the approximation of Eq. (2). In such form K is expressed in m^2. The calculation results shown in Figs. 3, 4

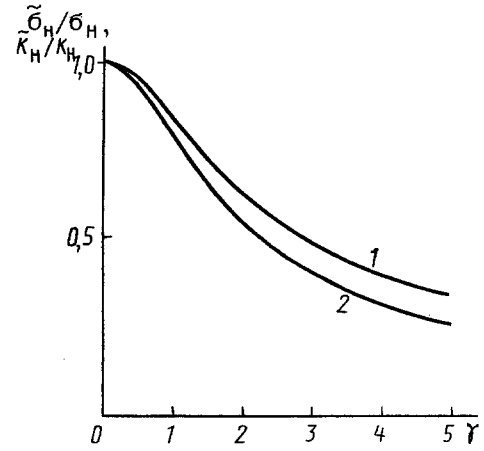

Fig. 2. Comparison of approximations of Eq. (2) with exact solution for single-cavity hyperboloid of revolution: 1) $\tilde{\sigma}_H/\sigma_H$; 2) $\tilde{K}_H/K_H$.

show that as $\varphi \to \varphi_c$, $\varphi > \varphi_c$, the calculated $1/\sigma$, $1/K \to \infty$ ($\varphi_c \approx 0{,}0349$ for the SC lattice, $\varphi_c \approx 0{,}0359$ for FCC and hexagonal). The experimental values are finite also for low φ ($\simeq 0.02$), which indicates small φ_c (apparently $\varphi_c < 0{,}02$) in real granular porous media. In a numerical modeling of overlapping spheres in an RCP lattice, [4] found a value φ_c (RCP) $\approx 0{,}03$. Among ordered lattices a significantly lower φ_c is found only in the volume centered lattice: $\varphi_c \approx 0.0055$. The low value of φ_c in real granular porous media may be related to several factors. Among these is scattering in grain dimensions. In the experiments of [2] the dispersion of grain dimensions was 20%, which probably led to denser packing, since the experiments of [7] indicate that in the presence of scattering over size the grain locations are more densely packed. Moreover, the low value of φ_c in other experiments may be related to a small addition (~3% of the total mass) of grains the size of which is much smaller than that of the main fraction. Lying in the pores between the coarse grains and forming an RCP lattice just like the coarse fraction, the fine fraction can reduce φ_c from a value of $\varphi_c \approx \varphi_c$ (RCP) ≈ 0.03 to $\varphi_c \approx (\varphi_c$ (RCP))$^2 \approx 0.001$. Finally, the smallness of φ_c may be controlled by sintering processes in the granular media.

In the ordered model considered in the critical region, i.e., for $0 < \dfrac{\varphi - \varphi_c}{\varphi_c} \ll 1$:

$$\sigma \sim (\varphi - \varphi_c)^{\tau}. \tag{12}$$

The value of τ may be obtained by expanding Eqs. (2) and (5) in the small parameter $(\varphi - \varphi_c)$ from Eq. (4). The quantity τ is determined by the geometry of the individual channel, namely the dependence $r(z)$ near $z = 0$, which has the form:

$$r(z) \approx \alpha + \beta z^m, \tag{13}$$

where β is a constant and the exponent $m = 2$ for the case of spherical grains considered. Equation (11) can be obtained from Eq. (5) as $z \to 0$. In the critical region $\alpha \sim (\varphi - \varphi_c)$, and the value of σ is determined by the integral

$$\frac{1}{g} \sim \int_0^c \frac{dz}{(\alpha + \beta z^m)^2}, \tag{14}$$

which diverges as $\alpha \to 0$ as $\alpha^{-\nu}$, where $\nu = 2 - 1/m$ (the value c of the upper limit in Eq. (14) is insignificant). For our case $m = 2$ and the exponent $\tau = 3/2$. This is also valid for the gas diffusion coefficient D in the pores for $\lambda \ll \alpha$. However, this relationship becomes unsatisfied as $\alpha \to 0$, where $\lambda \sim \alpha$. Therefore, in the quasi-Knudsen regime $D \sim \alpha(\varphi - \varphi_c)^{\tau} \sim (\varphi - \varphi_c)^{\tau+1}$. The gas permeability K may be calculated in analogy to the above, $K \sim (\varphi - \varphi_c)^{\tau+2}$.

In the model considered all pores have identical electrical conductivity g, and the structure is completely ordered. In real granular media with $\varphi \gg \varphi_c$ there exists some scattering in g values. Consideration of this fact does not lead to qualitative differences from the model described above, and $\sigma(\varphi)$ can be calculated for a concrete medium by the effective medium model of [8]. In the critical region the effect of nonorder in the lattice, related to disappearance of a significant portion of the pores due to pressing, proves significant: the value of τ in Eq. (12) differs from 3/2 (for spherical grains).

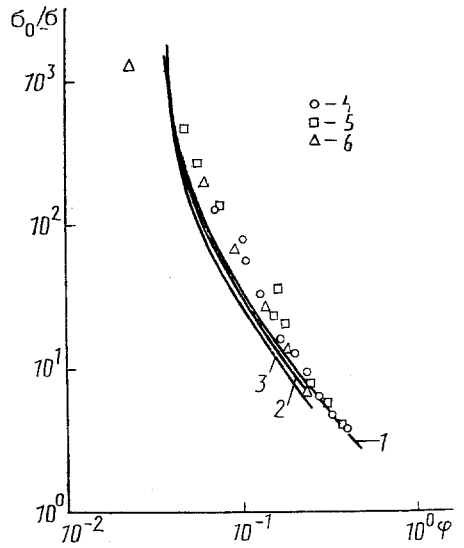

Fig. 3

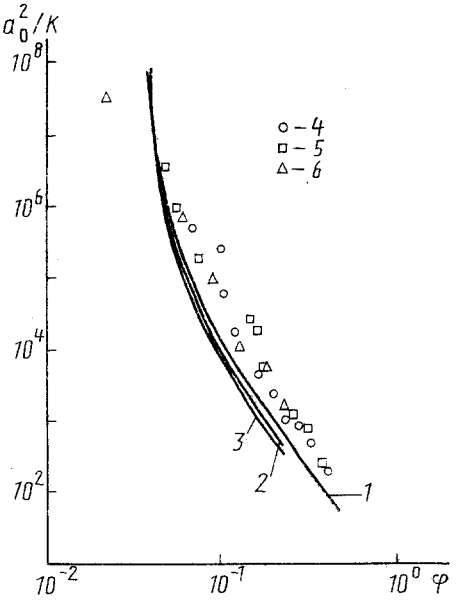

Fig. 4

Fig. 3. Comparison of calculation of electrical conductivity σ by Eq. (2) with experimental data of [2] (σ_0, intrinsic conductivity of electrolyte filling pores). Calculated curves: 1, SC lattice; 2, FCC; 3, hexagonal. Experimental points: 4, grain size 44-53 μm; 5, 88-106 μm; 6, 176-210 μm.

Fig. 4. Comparison of calculation of inverse gas permeability a_0^2/K by Eq. (2) with experimental data of [2]. Curves and points correspond to same lattices and grain size as in Fig. 3. Mean value within each grain group taken for a_0 in calculations.

To estimate τ in real granular medium we find the quantity p – the fraction of pores with g > 0 in the lattice of pores formed by the initial configuration of undeformed spheres (the pore lattice is determined by construction of Voronov polyhedra [4] around the grains). For large φ $p=1$, with decrease in φ there appear pores with g = 0 in a fraction $(1-p(\varphi))$. For $\varphi=\varphi_c$ $(p(\varphi_c)=p_c)$ the pore lattice ceases to be interconnected, $\sigma(\varphi_c)=0$. Realistic medium models lead to the relationship $(\varphi-\varphi_c)\sim(p-p_c)$ in the critical region. In percolation theory lattice problems for $0<\frac{p-p_c}{p_c}\ll 1$ $\sigma\sim(p-p_c)^t$. If the electrical conductivity of the pores g takes on two values 0 and g_1, i.e., the distribution function $f_g = (1 - p)\delta(0) + p\delta(g_1)$, then $t = t_u \approx 2.0$ [9]. However, as was shown in [10, 11], in the case where f_g has the form

$$f_g = (1-p)\,\delta(0) + p\frac{L}{g^{\omega}}, \tag{15}$$

the value $t = t_u + \omega/(1 - \omega)$ (in Eq. (15) $0 < \omega < 1$, the coefficient L being determined by normalization $\int f_g dg = 1$). To determine the form of f_g in the case of a granular porous medium we assume that the dimensions α of the pore channel throats are distributed over the range $0 \leq \alpha \leq \alpha_{max}$ with a distribution function $f_\alpha = (1 - p)\delta(0) + p\cdot\text{const}$ and that electrical conductivity of the channels $g \sim \alpha^\nu$ ($\nu = 2 - 1/m$, m being determined from Eq. (13)). Then, transforming from f_α to $f_g = f_\alpha \frac{d\alpha}{dg}$, we obtain for f_g the form of Eq. (15) with $\omega = 1 - 1/\nu$. This means that in the case of granular porous media with $m = 2, t = t_u + 1/2 \approx 2.5$, i.e., the index $\tau \approx 2.5$.

A more detailed treatment of the function $\sigma(\varphi)$ of an unordered lattice is possible if the model is concretized. However, the results of $\sigma(\varphi)$ calculation in such a model depend on the concrete details and comparison with experimental data is difficult.

In conclusion, we note that the simple $\sigma(\varphi)$ calculation considered above within the framework of an ordered model satisfactorily describes data for real granular porous media at not too large φ. However for a more exact description, together with the geometric characteristics of the pore channels contained in the ordered model considered above, the model of the porous medium should consider disorder of the pore lattice, which determines σ at low φ.

NOTATION

a, a_0, half the distance between sphere centers (a_0 corresponds to original location); A, B, parameters of single-cavity hyperboloid of revolution; c_0, L, constants; D, effective gas diffusion coefficient in porous medium; F, dimensionless gas permeability; f_g, f_α, pore distribution functions over electrical conductivity and throat radius; g, electrical conductivity of individual pore channel; h, ratio of surface radii of curvature; K, gas permeability of porous medium; K_H, $\tilde{K}_H$, approximate and exact gas permeability values for problem with single-cavity hyperboloid of revolution; k, gas permeability of individual porous channel; ℓ, m, t, t_u, ν, τ, ω, exponents in power laws; N, number of closest neighbors of sphere; P, gas pressure; p, fraction of bond-pores in pore lattice; R, radius of spherical grains; r, pore channel radius; S, cross-sectional area of channel; V, potential; $\partial/\partial n$, derivative along normal to the surface; v, gas velocity; w, ratio of pore surface area to material volume; x, y, z, coordinates; α, β, pore channel parameters; γ, hyperboloid parameter; η, gas viscosity; $\varkappa = R/a$; σ_0, electrical conductivity of electrolyte filling pores; σ, effective electrical conductivity of porous medium; σ_H, $\tilde{\sigma}_H$, quantities proportional to inverse of hyperboloid resistance (approximate and exact values); φ, porosity; φ_c, critical porosity value.

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